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HYDROSTATIC PRESSURE EFFECT ON T_c OF $Ba_{0.9}K_{0.1}Pb_{0.75}Bi_{0.25}O_3$

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The superconducting transition temperature of $Ba_{0.9}K_{0.1}Pb_{0.75}Bi_{0.25}O_3$ has been found to be suppressed smoothly by the application of hydrostatic pressure at a rate of $-(2.9 \pm 0.2) \times 10^{-5}\,\text{kbar}^{-1}$ up to 15 kbar. The implications of these results are discussed.

BOTH $BaPbO_3$[1] and $BaBiO_3$[2] exhibit perovskite-type structure but with slightly different symmetries.[3] They were recently found[3] to form a solid solution, $BaPb_{1-x}Bi_xO_3$, with Pb- and Bi-atoms occupying the octahedral sites. Wide range of electrical resistance behavior was also found[3] in this solution. The system is metallic for $x < 0.3$ while semiconducting otherwise. Superconductivity was observed in the composition range of $0.05 \leqslant x \leqslant 0.3$ with an onset transition temperature T_c increasing from ~ 9 K at $x = 0.05$ to ~ 13 K at $x = 0.3$ near the metal–semiconductor phase boundary. Samples with $x = 0$ and 0.35 are not superconducting down to 4.2 K. A T_c of 13 K in $BaPb_{1-x}Bi_xO_3$ system is the highest yet observed in compounds not containing any transition elements. The drastic variation of T_c with x was explained[3] in terms of the narrowing of the *s*-conduction band, consisting of the Pb- and Bi-6*s* states, as x increases. The semiconducting nature of the compounds with $x > 0.3$ was then attributed to the splitting of the 6*s*-conduction band and consequently the creation of a gap near the critical concentration.

The results of the present investigation show that: (1) *d*-electrons may have participated in the occurance of superconductivity in the $BaPb_{1-x}Bi_xO_3$ system, (2) the broad superconducting transition of the system seems likely to be caused by the concentration inhomogeneity near the metal–semiconductor phase boundary, and (3) the superconductivity in the system is a bulk effect.

Superconducting $BaPb_{1-x}Bi_xO_3$ compounds always show a broad transition.[3] However it has been demonstrated[3] that the substitution of 10–20% of the Ba in the compound by an alkaline element will sharpen the superconducting transition with little change in the onset of the transition temperature. Therefore high pressure study was carried out only on two powder samples of $Ba_{0.9}K_{0.1}Pb_{0.75}Bi_{0.25}O_3$. The procedure for sample preparation was previously described elsewhere.[3] The Pb–Bi composition of the samples examined was near the critical concentration where T_c is maximum and the concentration induced metal–semiconductor transition occurs. The superconducting transition was detected by a standard ac inductance bridge operating at 10 Hz. The temperature was determined by a Ge-thermometer. The hydrostatic pressure environment was provided by a self-clamp technique.[4] A fluid mixture of 1 : 1 *n*-pentane and isoamyl alcohol was used as the pressure medium. The reproducibility of T_c after immersing the sample in the pressure medium for a week indicated the high chemical stability of the sample in the pressure medium. The pressure at low temperature was measured by a Pb-manometer surrounded by the powder sample. The superconducting signal of one of the samples at atmospheric pressure was plotted in Fig. 1 as a function of temperature. The transition was still broad even with the K-substitution. The onset of the transition shown as a small maximum in the a.c. susceptibility curve was (11.73 ± 0.02) K, which is about 1 K lower than the maximum superconducting onset temperature previously reported[3] for the system. This can be caused by one or more of the following reasons: the slightly smaller x of the present samples, the possible difference in temperature calibrations and the different measuring techniques employed. The bulk of the transition occurs between 11 and 7 K as shown in Fig. 1. At 5.1 K, 95% of the sample was estimated to be superconducting. Further

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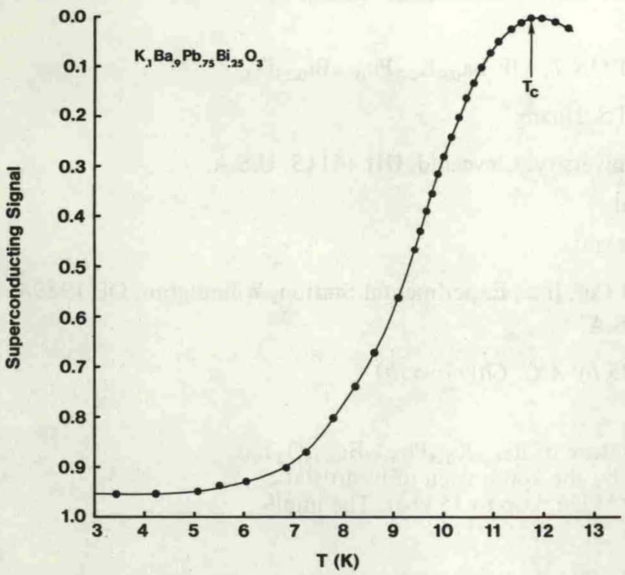

Fig. 1. Temperature dependence of the super conducting transition curve of a powder sample of $Ba_{0.9}K_{0.1}Pb_{0.75}Bi_{0.25}O_3$ as determined by an a.c. inductive method. The arrow defined the onset of the transition.

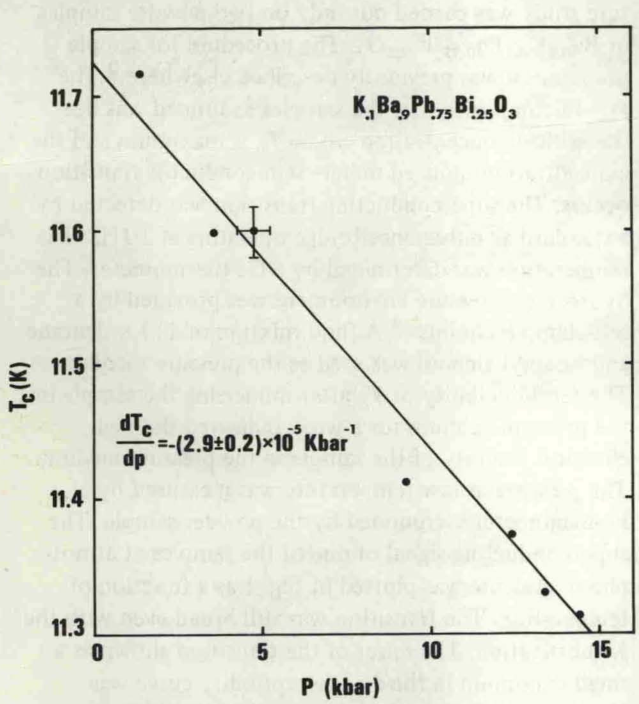

Fig. 2. Hydrostatic pressure effect on the onset temperature of the superconducting transition of $Ba_{0.9}K_{0.1}Pb_{0.75}Bi_{0.25}O_3$.

reduction in temperature did not increase the superconducting signal size. Because of the broad transition, hydrostatic pressure effect was determined only on the onset of the superconducting transition temperature T_c. The results were shown in Fig. 2. T_c decreases smoothly with pressure up to ~ 15 kbar at a rate of $-(2.9 \pm 0.2) \times 10^{-5}$ kbar^{-1}. The vertical bar represents the uncertainity in defining T_c. The same results were obtained for the other sample.

It has been demonstrated[5] that the volume effect on T_c can be expressed as $d \ln (T_c/\theta)/dV \equiv \phi \ln (\theta/T_c)$, where θ is the Debye temperature, V the volume and ϕ a material dependent constant. For nontransition metal (or *sp*) superconductors, $\phi \sim 2.5$, while for the transition metal (or *d*) superconductors, $\phi < 2.5$ and can become negative. The lack of knowledge on θ and the compressibility of $BaPb_{1-x}Bi_xO_3$ system prevents us from making use of this procedure to assess the different roles played by electrons in different bands. However an alternative approach was adopted. By examining all available data[5–7] on the relative pressure effect of T_c, i.e. $d \ln T_c/dP$, we found[8] that generally values of $d \ln T_c/dP$ fall into two groups with $d \ln T_c/dP < -8 \times 10^{-6}$ bar^{-1} for the *sp* superconductors, but $> -2 \times 10^{-6}$ bar^{-1} for superconductors with *d*-electrons in their conduction band, and the value is not sensitive to impurity except for cases where a pressure or impurity-induced Fermi surface topology change takes place. Since $d \ln T_c/dP$ for $Ba_{0.9}K_{0.1}Pb_{0.75}Bi_{0.25}O_3$ is -1.7×10^{-6} bar^{-1}, it is suggested that electrons from the *d*-band may contribute significantly to the high T_c of the system due to the $5d$–$2p$ and/or $5d$–$6s$ hybridizations and the system may show a large critical field.

The abrupt disappearance of superconductivity following the T_c-peak strongly suggests a drastic change in the electron energy spectrum of $BaPb_{1-x}Bi_xO_3$ as x becomes larger than ~ 0.3, inspite of the fact[3] that no no apparent anomaly was detected at $x \sim 0.3$ in the size of the pseudocubic cell of the system. This makes it all the more tempting to propose that the metal–semiconductor transition is electronic in nature. Such an electronic instability can be due to the large density of state which varies drastically with concentration or the particular shape of the Fermi surface of the system near the critical concentration. This would result in the splitting of the conduction band and the creation of an energy gap associated with the semiconducting phase, as previously suggested.[3] The broad superconducting transition of the system can then be easily attributed to a concentration inhomogeniety (or fluctuation) near the metal–semiconductor phase boundary, instead of any internal strain due to the possible presence of a small two phase region near the critical concentration in view of the small pressure effect on T_c observed. Experiments to provide further evidence are in progress.

Finally, we would like to point out that all known high T_c oxide systems ($BaPb_{1-x}Bi_xO_3$,[3] $Li_{1+x}Ti_{2-x}O_4$,[9] A_xWO_3,[10] with A as an alkaline or alkaline earth atom) have the following in common: (1) superconductivity occurs only over a limited range of x, and the superconducting phase usually is sandwiched between a conducting and a semiconducting phase, (2) T_c increases rapidly as x approaches the semiconducting phase boundary and disappears abruptly beyond the phase boundary, and (3) they all have atoms occupying the octahedral sites with six oxygen nearest neighbors. Further study is under way way to look for possible pressure or temperature induced electronic transition in $BaPb_{1-x}Bi_xO_3$ and to understand the causes responsible for the peculiar superconducting behavior in these high T_c oxide systems.

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